

Hartree-Fock approximation for multi-electron atoms.

Start with the Slater determinant for  $N$  atoms:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \dots & \varphi_1(N) \\ \vdots & & \vdots \\ \varphi_N(1) & \dots & \varphi_N(N) \end{vmatrix}$$

where  $\varphi_i(j)$  means  $\varphi_i(\vec{r}_j, m_j)$   $j=1,\dots,N$   
 $\leftarrow S_z$  e-value: suppress

and the  $\varphi_i$  are orthonormal trial wavefunctions.

The expectation value of  $H$  in this state is:

$$\langle \Psi | H | \Psi \rangle = - \sum_{i=1}^N \int d^3\vec{r} \left[ \frac{1}{2m} |\nabla \varphi_i(\vec{r})|^2 + \frac{Ze^2}{r} |\varphi_i(\vec{r})|^2 \right]$$

$$+ \frac{1}{2} \sum_i \sum_{j \substack{(i \neq j)}} \int d^3\vec{r} \int d^3\vec{r}' \frac{e^2}{|\vec{r}-\vec{r}'|} \left\{ |\varphi_i(\vec{r})|^2 |\varphi_j(\vec{r}')|^2 \right. \\ \left. - \delta_{s_i s_j} \varphi_i^*(\vec{r}) \varphi_i(\vec{r}') \varphi_j^*(\vec{r}') \varphi_j(\vec{r}) \right\}$$

$\uparrow$  only contributes for same spin  $\leftarrow$  exchange energy

Use variational principle to minimize w.r.t.  $\varphi_i$ .

Solution: solve coupled, non-linear e-value equations:

$$\left( -\frac{\nabla^2}{2m} - \frac{Ze^2}{r} \right) \varphi_i(\vec{r}) + \int d^3\vec{r}' \frac{e^2}{|\vec{r}-\vec{r}'|} \left\{ \varphi_i(\vec{r}) |\varphi_j(\vec{r}')|^2 - \delta_{s_i s_j} \varphi_i(\vec{r}') \varphi_j(\vec{r}) \varphi_j^*(\vec{r}') \right\}$$

$$= \epsilon_i \varphi_i(\vec{r})$$

Assume that the  $\varphi_i$  are approximately determined by some spherical potential. Then

$$\varphi_i(\vec{r}) = \underbrace{R_{nl}(r)}_{\left\{ \right.} \underbrace{Y_{lm}(\theta, \varphi)}_{\text{known}} \chi_{m_s} = \text{orbitals}$$

Not same as hydrogen atom, but does have  $n-l-1$  nodes.

Orbitals are labelled by  $n, l, m_l, m_s$ .

The eigenvalues  $E_i$  are approximately  $-(\text{energy})$  needed to remove an electron from the  $i$ th orbital. (Neglects change in other orbitals when  $i$ 'th electron removed.)

$E_i$  increases with  $n$ . (Also depends on  $l$ , unlike Hydrogen atom.)

To specify an atomic state:

- 1) Give the electron configuration, say  $(1s)^2 (2s)^2 (2p)^2$  for Carbon  
 $(1s)^2 (2s)^2 (2p)^3$  for Nitrogen

For a given  $n$ , smaller  $l$  states have lower energy.

(Electrons with smaller  $l$  closer to nucleus, inside screening cloud due to other electrons.)

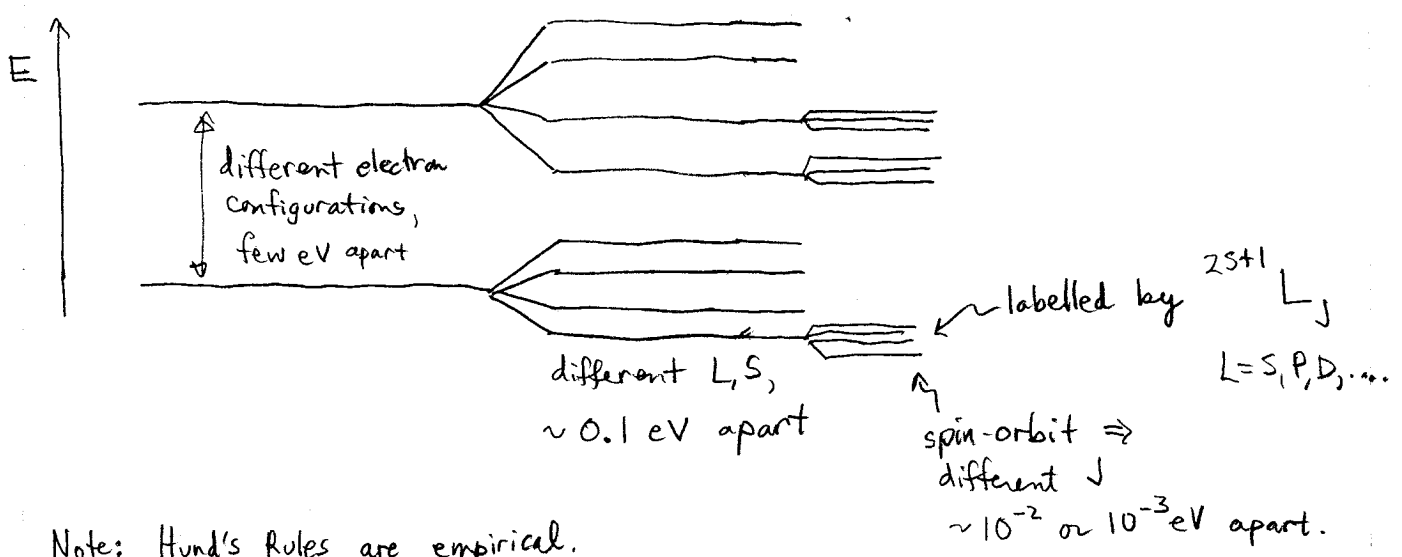
- 2) Give  $L$  and  $S$  = eigenvalues of total angular momentum, spin

Hund's Rules: For a fixed electron configuration,

- 1) The  $LS$  multiplet with largest  $S$  has lowest energy.
- 2) If several  $L$ 's have same  $S$ , the largest  $L$  has the lowest energy.

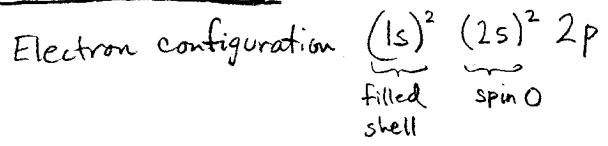
- 3) Within each  $LS$  multiplet, spin-orbit coupling splits apart different levels of  $J = |L-S|, \dots, L+S$ .

Hund's Rule 3) If the incomplete shell  $\leq$  half-filled, then ground state has  $J = |L-S|$ , otherwise  $J = L+S$ .



Note: Hund's Rules are empirical.

Example: Boron has 5 electrons.

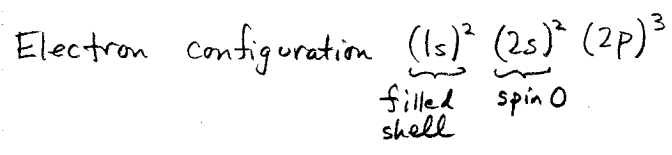


(Note 2s fills first.)

In the unfilled shell, have  $L=1, S=1/2$ . So  $^{2S+1}L_J = {}^2P_{1/2}, {}^2P_{3/2}$ .  
 only possibility; don't need Hund's rules 1, 2.

The  $n=2$  shell has  $2 \sum_{l=0}^{n-1} (2l+1) = 2(1) + 2(3) = 8$  possible states, of which 3 are filled. So Hund rule 3 says J is minimized, and  ${}^2P_{1/2}$  is the ground state.

Example: Nitrogen has 7 electrons.



So the problem reduces to identifying the  $(2p)^3$  state for L, S, J.  
 How many such states are there? Each 2p orbital has  $2(2l+1) = 6$  possible states.

Antisymmetrize 3 electrons:  $\frac{6 \cdot 5 \cdot 4}{3 \cdot 2 \cdot 1} = 20$  total  $(2p)^3$  states.

Naively:  $L = 0, 1, 2, 3$ , and  $S = 1/2, 3/2$ .

But, if  $L=3$ , the spatial wavefunction is totally symmetric, and there is no totally antisymmetric spin state for 3 electrons. So  $L \neq 3$ .

Also, if  $L=0$ , the spatial wavefunction is totally antisymmetric, so the spins must be totally symmetric  $\Rightarrow S = 3/2$ .

Conversely, if  $S = 3/2$  (totally symmetric spins) then only  $L=0$  is allowed. So, the allowed L, S levels are:

$L=2, S=1/2$	$L=1, S=1/2$	$L=0, S=3/2$
$(5 \cdot 2 = 10 \text{ states})$	$(3 \cdot 2 = 6 \text{ states})$	$(1 \cdot 4 = 4 \text{ states})$

Hund's Rule says  $L=0, S=3/2$  wins.

Taking into account spin orbit coupling, we have:

${}^2D_{3/2}, {}^2D_{5/2}$        ${}^2P_{1/2}, {}^2P_{3/2}$        ${}^4S_{3/2}$  ← The lowest energy.